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(54) **An atmospheric plasma reaction method and a device therefor**

Verfahren und Gerät zur Plasmabehandlung unter atmosphärischem Druck

Méthode et appareil de traitement par plasma sous pression atmosphérique

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Description

The present invention relates to an atmospheric plasma reaction method and the device therefor. More particularly, this invention relates to an atmospheric plasma reaction method and the device therefor wherein stable glow discharge plasma is caused to generate under atmospheric pressure, and also the active species generated by this atmospheric plasma is transported to the downstream for treating the surface and/or forming a thin film on a large-size substrate.

Conventionally, a film-forming or surface treatment method with low pressure glow discharge plasma has been widely known, and has found extensive applications in various industrial fields. As the surface treatment method with low-pressure glow discharge plasma, the so-called plasma etching method that an etching and a thin film formation are made by the plasmatization of reactive gases including halogen atoms and silicon atoms, and the deposit method are known.

Such plasma etching method and deposit method include etching of silicon and oxidated silicon film with Freon gas and other carbonfluoride plasma in a vacuum container, and depositing of amorphous silicon film, oxidated silicon film or nitride silicon film onto a silicon substrate or glass substrate by plasma-exciting silane gas or a mixed gas of oxygen or ammonia gas therewith.

However, the surface treatment methods of low-pressure glow discharge plasma as has conventionally been known, use reactions under vacuum of some $1x10^{-2}$ - 1 Torr, and hence a device and equipment for forming these low-pressure conditions were required. It was also difficult to treat a large-area substrate and the production cost was inevitably high.

One of the inventors to the present invention has already proposed a plasma reaction method for plasma exciting monomer gas introduced in a mixed gas with rare gas under atmospheric pressure and treating the surface of a substrate (See JOURNAL OF PHYSICS D: APPLIED PHYSICS, vol. 21, no. 21, May 14, 1988, Letchworth, GB, pages 838-840; Kanazawa, S. et al.: "Stable glow plasma at atmospheric pressure"). He has put this method into application, achieving a surface with superb characteristics and functions. However, there was a limit to the treatment of surface even by this method, and particularly in the case where a gas is metal or alloy, are discharge occurred under atmospheric pressure, making the treatment difficult. In addition, the treatment area depends on the area of an electrode, and hence it was difficult to treat a large area.

The present invention has been made considering the aforestated circumstances, and is a further expansion of the method already proposed. It has an objective of providing an atmospheric plasma reaction method and the device therefor which can give plasma with reaction activity and stability under atmospheric pressure, without any arc discharge occurring even in the case where the substrate is a metal or an alloy or it is a large area substrate.

This invention provides a method of treating a surface of a substrate according to claim 1 and an atmospheric plasma reaction device, according to claim 3.

Fig. 1 is a sectional view illustrating one of the embodiments of an atmosphere plasma reaction device of this invention.

Fig. 2 is a perspective view illustrating the structure of a dielectric-coated electrode.

Fig. 3 is a perspective view illustrating another embodiment of an atmosphere plasma reaction device of this invention.

Figs. 4 and 5 are correlation drawings which show the relationships between the etching speed of Si and SiO_2 at substrate temperatures of 100°C and 20°C and the concentration of O_2 in CF_4.

Fig. 6 is a correlation drawing showing the relationships between the etching speeds of Si and SiO_2 and substrate temperatures.

Fig. 7 is a correlation drawing showing the relationships between the etching speeds of Si and SiO_2 and the location of the substrates.

In an atmospheric plasma reaction method according to the present invention and the device therefor, a mixed gas of rare gas with reactive gas is used, and dielectric-coated electrodes with which a solid dielectric is provided are located perpendicular to a substrate, and a surface treatment portion for supporting a substrate and treating the surface thereof is provided downstream of the plasma-generating portion of an atmospheric plasma generating unit making possible stable glow discharge and the surface-treatment of a large-area substrate. Even where the substrates a metal or an alloy, stable glow discharge can be obtained, and where it is a large-area substrate, the surface treatment can be ensured.

Detailed descriptions will be made as to the embodiments of this invention while referring to the drawings.

Fig. 1 is a sectional view of one of the embodiments illustrating an atmospheric plasma reaction device of this invention.

As shown in this example, the device according to the present invention comprises a gas introducing unit (3) for introducing mixed gas (1) of rare gas and reactive gas into a rection vessel (2) consisting of Teflon plate and which is kept at atmospheric pressure, an atmospheric plasma generating unit (8) wherein dielectric-coated electrodes (6) with a solid dielectric (5) provided on the surfaces of two or more electrodes (4) are located parallel with each other is located perpendicular to a substrate (7) and a surface treatment unit (9) which supports the substrate (7) downstream of the plasma generating portion of that atmospheric plasma generating unit (8) and treats the surface thereof with the active specifies generated.

Generally, glow discharge will not occur readily under atmospheric conditions. Arc discharge is occured by applying high voltage, and hence it becomes difficult to

perform the surface treatment of a substrate.

In this invention, however, glow discharge under atmospheric pressures is made possible by using a mixed gas (1) of reactive gas with rare gas, locating dielectric-coated electrodes (6) with solid dielectrics (4) provided with electrodes (5) perpendicular to a substrate (7), and providing a surface treatment unit (9) for supporting the substrate (7) downstream of the plasma generating region of the atmosphere plasma generating unit (8).

Even when the substrate (7) is a metal or an alloy, a stable glow discharge can be obtained, and even when it is a large-area plate, the surface treatment of said substrate can be ensured. There is no need to say that when the substrate is of ceramics, glass, plastic and rubber, stable glow discharge is ensured and a substrate of large area can be subject to surface treatment.

Fig. 2 illustrates the structure of dielectric coated electrodes (6) located in an atmosphere plasma generating unit (8) which excites a mixed gas (1) of rare gas and reactive gas under atmospheric pressures.

In this example, a total of four electrodes parallel plate ground electrodes (41) two pairs each provided parallel with each other are used. A high-frequency electric field is applied from a high-frequency power suply (11) to the high-frequency electrodes (42) via a matching device (10). The both sides of each of these electrodes (41)(42) are provided with a solid dielectric field (5). The materials of the solid dielectric field (5) include glass, ceramics, plastic and other heat-resistant materials.

A mixed gas of rare gas and reactive gas is excited with glow discharge using such dielectric-coated electrodes (6), generating high-energy plasma. The formation of this plasma is provided by the application of high voltage from the high-frequency power supply (11). The voltage applied at that time may be arbitrary depending on the property of the surface of the substrate and the time for which the surface is treated.

There is no special limitation to the number of electrodes, but any number of two or more is acceptable. Nor is there any specific limitation to the materials of the electrodes (41)(42). Stainless steel and other given material may be used.

As illustrated in Fig. 1, a mixed gas (1) of rare gas and reactive gas is introduced into a reaction vessel (2) through a gas introducing port (12) provided on the reaction vesel (2), passes through a space (13) and is dispersed evenly at an atmosphere plasma generating unit (8). Gases from a reaction product, unracted portion of reactive gas and rare gas are discharged via an exhaust port (15).

To obtain more stable plasma at atmospheric pressure, it is preferred to disperse and supply a mixed gas (1) of rare gas and reactive gas to the plasma generating region in the vicinity of dielectric-coated electrodes (6). For this reason, in this example, a multi-port plate (16) is also provided.

At a substrate support (14), a temperature sensor (17) which measures the temperature of the substrate (7) of a thermocouple, a heater (18) for heating the substrate (7), and a water-cooled pipe (19) for cooling the substrate (7), are also provided. These means may be arbitrarily provided.

There is no specific limitation to a mixed gas (1), but as rare gas to be used, He, Ne and Ar can used singularly or in combination with other substances. To prevent arc discharge and provide stable glow discharge, it is preferred to use He, a gas with light mass. For reactive gases to be introduced in combination with rare gases, silicon hydrogases such as silane (SiH_4) and disilane (Si_2H_6) or halogenated hydrocarbon including CF_4, C_2F_5, CHF_3 or SF_5 and hydrocarbons with or without other functional groups may be used arbitrarily. Reactive gases with multiple species can be mixed and used for that application. Furthermore, depending on the reactive gases to be used, halogen, oxygen, and hydrogen may be added to the mixed gas to accelerate a reaction. There is no specific limitation to the mixing ratio of rare gas with reactive gas, but it is preferred to make the density of rare gas about 65% or higher, especially 90% or higher.

When these gases used for a reaction are released into the atmosphere, there are some cases where they will cause safety problems including fire and undesirble effects upon the human body. In order to avoid this cases, it becomes necessary to detoxify these gases. Since the gases such as He are expensive, it is prefered to collect them for reuse. Given these, the device of this invention can be covered with a separate container (21) from the reaction vessel (2) which is used to isolate a plasma reaction system from atmosphere. Using a pump and other appropriate exhaust means connected to the isolation container (21), the pressure inside can be reduced to approx. 0.5 to 0.1 atmospheric pressure. The discharge mechanism for this is identical to that under atmospheric pressure.

According to the type and reaction conditions of reactive gases to be used, plasma polymer film, deposit film, plasma treatment film or plasma etching surface can be obtained.

Fig. 3 is a perspective diagram of another example of the atmosphere plasma reaction device of this invention.

In this example, a pair of dielectric-coated electrodes (6) with a solid dielectric (5) provided on one of the sides of the electrodes (4) and longer in the cross direction of a substrate (20) are provided inside a convex reaction vessel (2), so that the substrate (20) is scanned in the directions of an arrow (x) and/or an arrow (y). This ensures that if the substrate (20) is a large-area substrate, the surface can be treated. When this device is used for surface treatment, it is preferrd to scan the substrate (20) in both directions of the arrows (x)(y) to provide more evenly treated surface.

In this case also, to prevent the gases from dispersing into the atmosphere, the whole device can be cov-

ered by an isolation container different from the reaction vessel (2). With an appropriate exhaust means such as a pump, the internal pressure can be reduced to approx. 0.5 to 0.1 atmospheric pressure. The discharge mechanism for this operation is similar to that under atmospheric pressure.

Now, Description will be made as to the specific examples of surface treatment.

Treamtment Example 1

In a device as descried in Fig. 1 wherein four plate electrodes with a shape of square having a 30 mm side are used, and glass plate-coated electrodes, located parallel with each other in a clearance of 4 mm, were provided at an atmosphere plasma generating portion, 1 cm^2 single crystal silicon (100) and thermally oxidated film were provided 1 cm apart from the bottom of the dielectric-coated electrodes. These substances were heated to 100°C to vary the concentration of O_2 into CF_4 for plasma etching. The total flow of $CF_4 + O_2$ was kept constant at 25 sccm, and the flow rate of He at 4×10^3 sccm. A high-frequency power at 13.56 MH_2 was set at 70 V. The result is show in Fig. 4.

The single crystal silicon and thermal treated film were subject to etching. The etching speed was approx. 2.5 heat $(CF_4 + O_2)/O_2$ ratio, i.e., it was confirmed that when CF_4 was approx. 30 cc and O_2 was some 70 cc, the silicon (S1) and the oxidated film (SiO_2) attained the maximum etching speed.

During the etching operation, no arc discharge occured, and glow discharge ocurred under stable atmospheric pressures, giving highly active plasma.

Temperature Example 2

Under the same condition as in Example 1, except for setting the temperature of the substrate at 20°C, a single crystal silicon and thermally oxidated film were subject to etching. The result is show in in Fig. 5. As is shown by a comparison with Fig. 4, it was found that the etching speed of the silicon (Si) does not change greatly with substrate temperatures, but that the etching speed of oxidated film (SiO_2) decreases substantially, improving the selection ratio of Si/SiO_2 more than 15 times.

In this case also, no arc discharge occurred and glow discharge occurred under stable atmospheric pressures, giving highly active plasma.

Treatment Example 3

Keeping the flowrate ration $(CF_4 + O_2)/O_2$ at 3 and varying substrate temperatures, the etching speed of a single crystal silicon and thermally oxidated film were observed. The result is indicate in Fig. 6.

The single crystal silicon and thermally oxidated film was subject to etching. As is evident from Fig. 6, it was confirmed that the selection ratio of Si/SiO_2 became enormously larger as the substrate was cooled.

In this case also, during the etching operation, glow discharge occurred, giving highly active plasma. No arc discharge occurred.

Treatment Example 4

Under similar conditions as in Example 3 and varying the location of the substrates with regard to dielectric-coated electrodes, the etching speed of the silicon (Si) and thermally oxidated film (SiO_2) was observed. The location of the substrate in this case was further apart from those in Example 1 to 3.

It was determined that the etching speeds of both the silicon (Si) and thermally oxidated film (SiO_2) decrease as they are more distant from the dielectric-coated electrodes, but that an effective etching speed was achievable even when those substrates are 3 cm distant from the electrodes.

The present invention is not limited to the above examples. Various configurations can be realized depending on the geometry, size and material of a reaction vessel, the construction and structure of a dielectric-coated electrode, the type and flowrate of rare gas and reactive gas, the quantity of applied power, substrate temperature, and the location and distance of the substrate from the dielectric-coated electrodes.

When the pressure inside the container is to be reduced for the exhaust and disposal of reactive gas and reaction production and the collection of He and other rare gases, the discharge machanism become similar one under the atmospheric pressure.

As has been described in detail, this invention makes unnecessary the device and equipment for the formation of vacuum systems, reduces cost, and achieves surface treatment under the atmospheric pressures, as compared with the conventional low-pressure glow discharge plasma reaction method. Since the structure and construction of the device are simple, it becomes easier to perform surface treatment of large-area substrate. The desired surface treatment can be obtainted regardless of the materials and size of the substrate.

Claims

1. A method of treating a surface of a substrate (7) comprising introducing a mixed gas (1) of rare gas and reactive gas into a reaction vessel (2)

   exciting said mixed gas of gases with plasma at atmospheric pressure, and treating the surface of a substrate with the active species thereby generated, characterised in that
   the excitation of said mixed gas is achieved by passing said mixed gas through an atmospheric plasma generation region (8) comprising di-

electric-coated electrodes (6) wherein the surface of two or more of the electrodes (4) have solid dielectrics (5) and are located parallel with each other, said dielectric-coated electrodes (6) being located perpendicular to the substrate (7), and said surface treatment is carried out downstream of all of said dielectric-coated electrodes (6).

2. A method as claimed in Claim 1 wherein the surface of the substrate is treated with reactive gas comprising halogen atoms.

3. An atmospheric plasma reaction device comprising

a reaction vessel (2),
gas-introducing means for introducing a mixed gas (1) of rare gas and reactive gas into said reaction vessel (2),
an atmospheric plasma generation unit, and a a surface treatment unit for treating the surface of a substrate (7), characterised in that
the atmospheric plasma generation unit (8) comprises dielectric-coated electrodes (6) wherein the surface of two or more of the electrodes (4) have solid dielectrics (5) and are located parallel with each other, said dielectric-coated electrodes (6) being located perpendicular to the substrate (7), and
the surface treatment unit (9) is downstream of the atmospheric plasma generation unit (8).

4. An atmospheric plasma reaction device as claimed in Claim 3 wherein an isolation vessel is provided to reduce the pressure to 1/10 atmospheric pressure.

Patentansprüche

1. Verfahren zur Oberflächenbehandlung eines Substrates (7) mit den Schritten:

Einführen eines Gasgemisches (1) aus Edelgas und Reaktionsgas in ein Reaktionsgefäß (2),
Anregen des Gasgemisches durch Plasma bei atmosphärischem Druck und Behandeln einer Substratoberfläche mit der dadurch hergestellten aktiven Verbindung,

dadurch gekennzeichnet, daß

die Anregung des Gasgemisches dadurch erreicht wird, daß man das Gasgemisch durch einen Bereich (8) führt, wo unter atmosphärischem Druck Plasma erzeugt wird, welcher mit Dielektrikum beschichtete Elektroden (6) umfaßt, wobei die Oberfläche von mindestens zwei der Elektroden (4) feste Dielektrika (5) aufweisen und parallel zueinander angeordnet sind, wobei die mit Dielektrikum beschichteten Elektroden (6) senkrecht zu dem Substrat (7) angeordnet sind und die Oberflächenbehandlung stromabwärts von sämtlichen mit Dielektrikum beschichteten Elektroden (6) durchgeführt wird.

2. Verfahren gemäß Anspruch 1, wobei die Substratoberfläche mit Reaktionsgas behandelt wird, das Halogenatome umfaßt.

3. Vorrichtung für Plasmareaktionen bei atmosphärischem Druck, mit

einem Reaktionsgefäß (2),
Einführungsmitteln zum Einführen eines Gasgemisches (1) aus Edelgas und Reaktionsgas in das Reaktionsgefäß (2),
einer Einheit zur Plasmaerzeugung bei atmosphärischem Druck und einer Oberflächenbehandlungseinheit zur Behandlung der Oberfläche eines Substrates (7), dadurch gekennzeichnet, daß
die Einheit (8) zur Plasmaerzeugung bei atmosphärischem Druck mit Dielektrikum beschichtete Elektroden (6) umfaßt, wobei die Oberfläche von mindestens zwei der Elektroden (4) feste Dielektrika (5) aufweisen und parallel zueinander angeordnet sind, wobei die mit Dielektrikum beschichteten Elektroden (6) senkrecht zu dem Substrat (7) angeordnet sind, und
die Oberflächenbehandlungseinheit (9) sich stromabwärts der Einheit (8) zur Plasmaerzeugung bei atmosphärischem Druck befindet.

4. Vorrichtung für Plasmareaktionen bei atmosphärischem Druck gemäß Anspruch 3, wobei ein Isolationsgefäß zur Verringerung des Drucks auf 1/10 Atmosphärendruck vorgesehen ist.

Revendications

1. Procédé pour traiter une surface d'un substrat (7), comprenant les étapes consistant à introduire un mélange gazeux (1) d'un gaz rare et d'un gaz réactif dans une enceinte réactionnelle (2), exciter ledit mélange de gaz avec un plasma à la pression atmosphérique, et traiter la surface d'un substrat avec les espèces actives ainsi produites,
caractérisé en ce que
l'excitation dudit mélange gazeux est réalisée en faisant passer ledit mélange gazeux à travers une région (8) de production d'un plasma atmosphérique, comprenant des électrodes (6) recouver-

tes d'un diélectrique, les surfaces de deux des électrodes (4) ou plus comportant des diélectriques solides (5) et étant parallèles entre elles, lesdites électrodes (6) recouvertes de diélectrique étant disposées perpendiculairement au substrat (7), et ledit traitement de surface est exécuté en aval de l'ensemble desdites électrodes (6) recouvertes de diélectrique.

2. Procédé selon la revendication 1, selon lequel la surface du substrat est traitée avec un gaz réactif comprenant des atomes d'halogène.

3. Dispositif de réaction plasmatique atmosphérique comprenant

une enceinte réactionnelle (2),
des moyens d'introduction d'un gaz servant à introduire un mélange gazeux (1) d'un gaz rare et d'un gaz réactif dans ladite enceinte réactionnelle (2),
une unité de production de plasma atmosphérique, et
une unité de traitement de surface pour traiter la surface d'un substrat (7),

caractérisé en ce que

l'unité (8) de production de plasma atmosphérique comprend des électrodes (6) recouvertes d'un diélectrique, les surfaces de deux des électrodes (4) ou plus comportant un diélectrique solide (5) et étant parallèles entre elles, lesdites électrodes (6) recouvertes de diélectrique étant disposées perpendiculairement au substrat (7), et
l'unité de traitement de surface (9) est disposée en aval de l'unité (8) de production de plasma atmosphérique.

4. Dispositif de réaction plasmatique à la pression atmosphérique selon la revendication 3, dans lequel une enceinte isolante est prévue pour réduire la pression à 1/10 de la pression atmosphérique.

FIG. 1

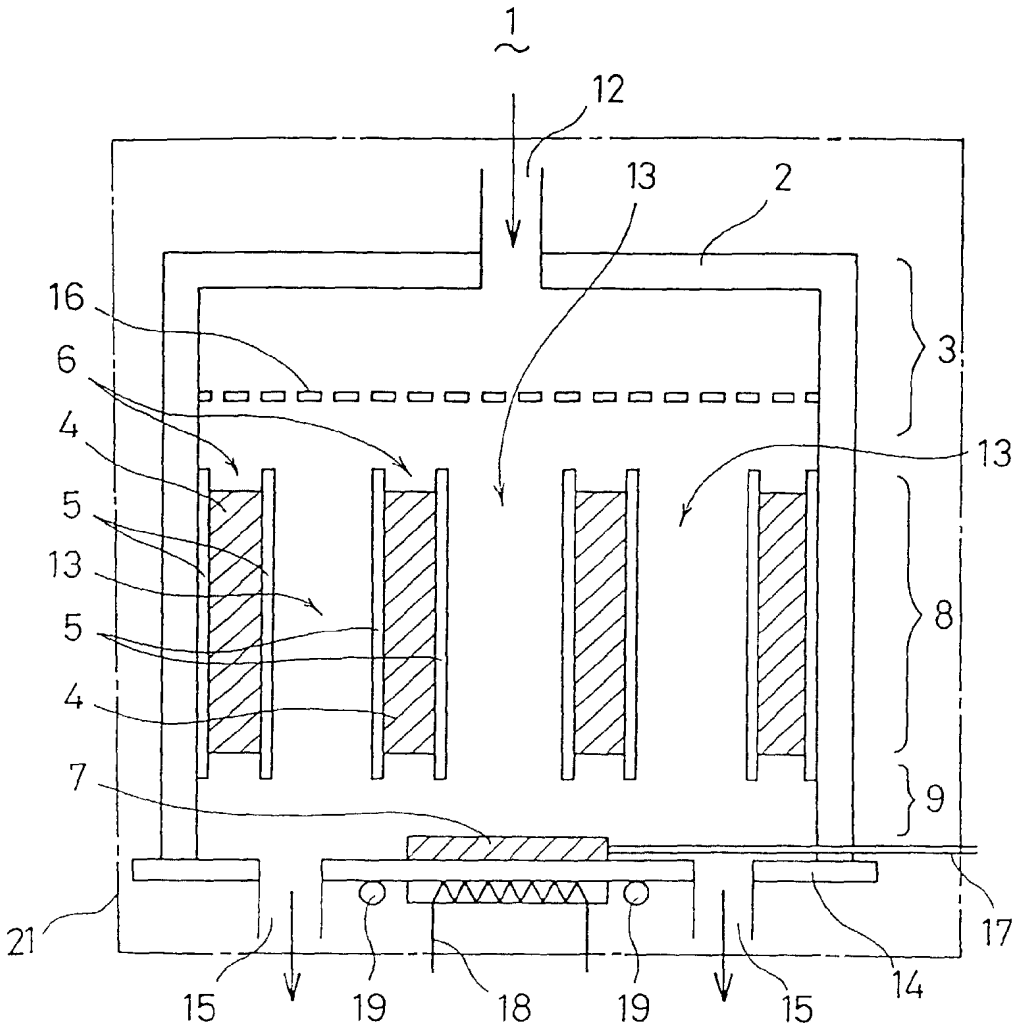


FIG. 2

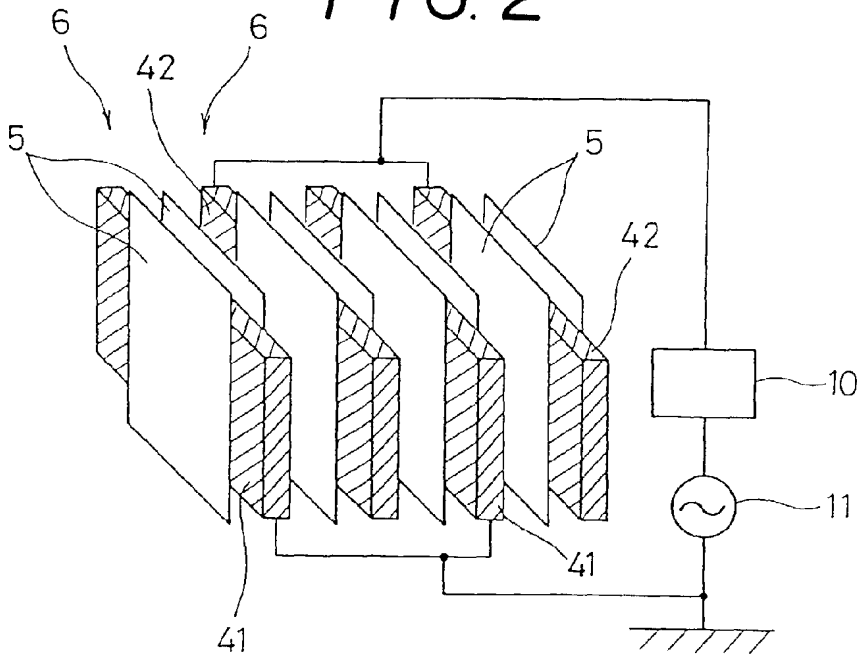


FIG. 3

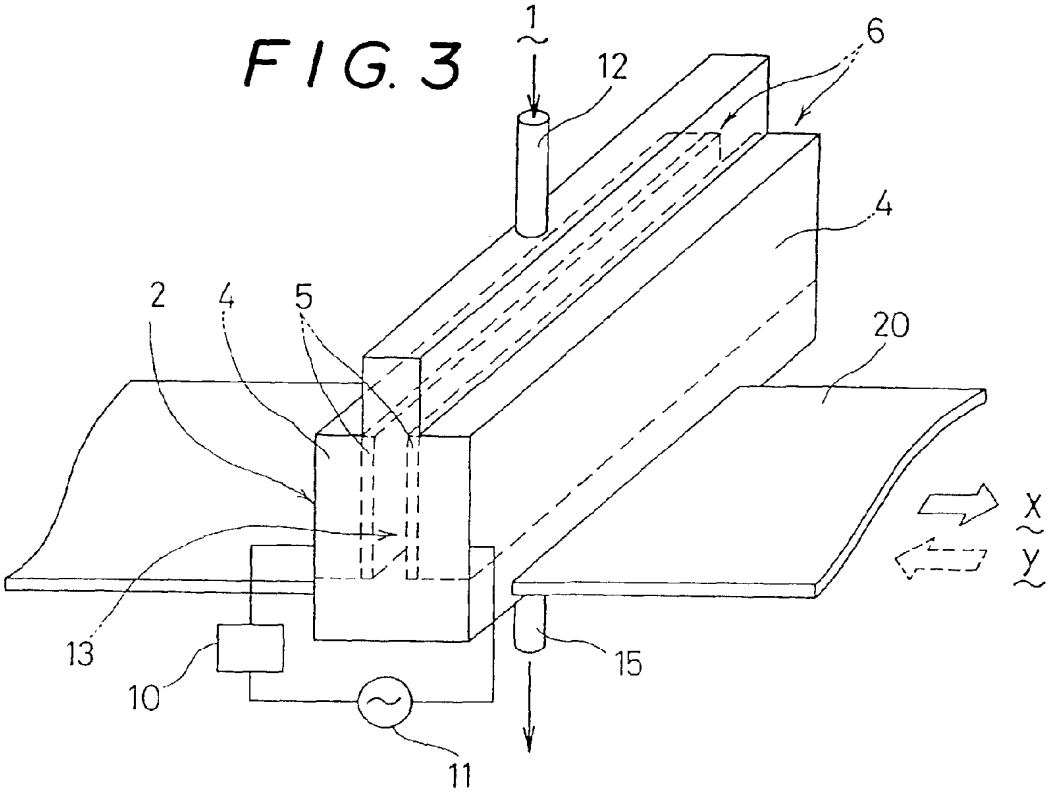


FIG. 4

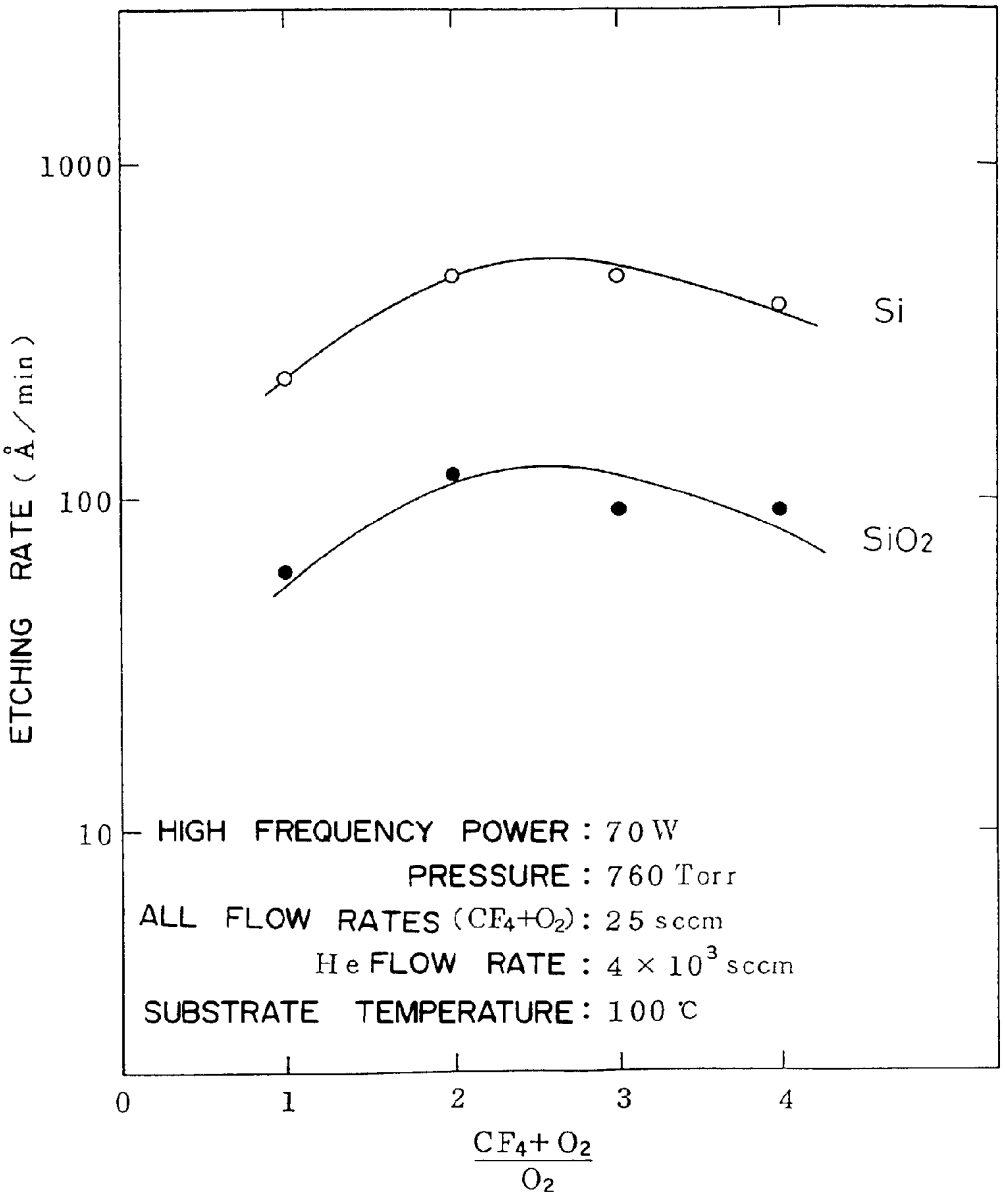

1000
100
10
ETCHING RATE (Å/min)
Si
SiO2
HIGH FREQUENCY POWER : 70 W
PRESSURE : 760 Torr
ALL FLOW RATES (CF4+O2) : 25 sccm
He FLOW RATE : 4 × 10^3 sccm
SUBSTRATE TEMPERATURE : 100 ℃
0
1
2
3
4
CF4+O2 / O2

FIG. 5

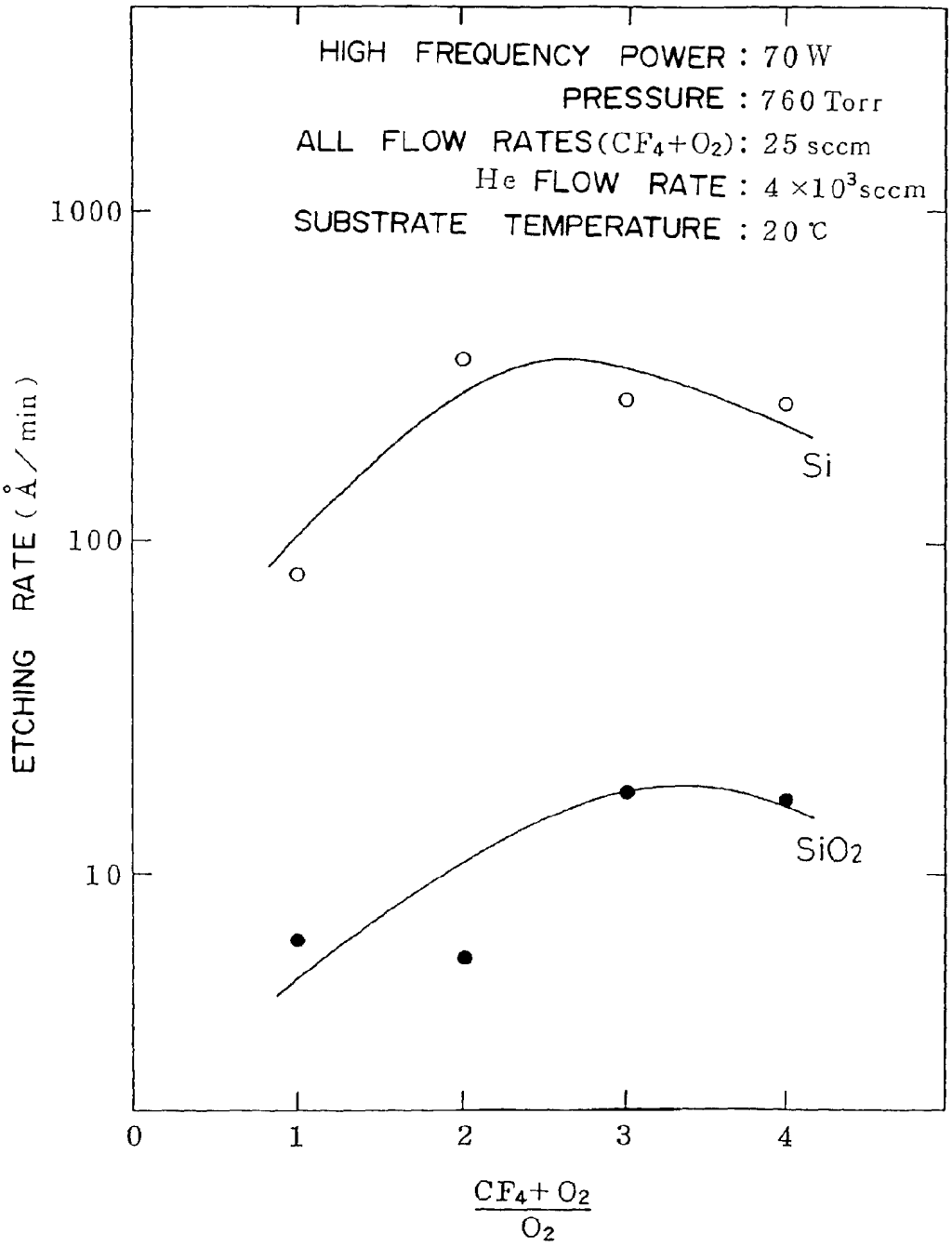

HIGH FREQUENCY POWER : 70 W
PRESSURE : 760 Torr
ALL FLOW RATES (CF_4+O_2) : 25 sccm
He FLOW RATE : 4×10^3 sccm
SUBSTRATE TEMPERATURE : 20 ℃
ETCHING RATE (Å/min)
1000
100
10
Si
SiO_2
0
1
2
3
4
$\frac{CF_4+O_2}{O_2}$

FIG. 6

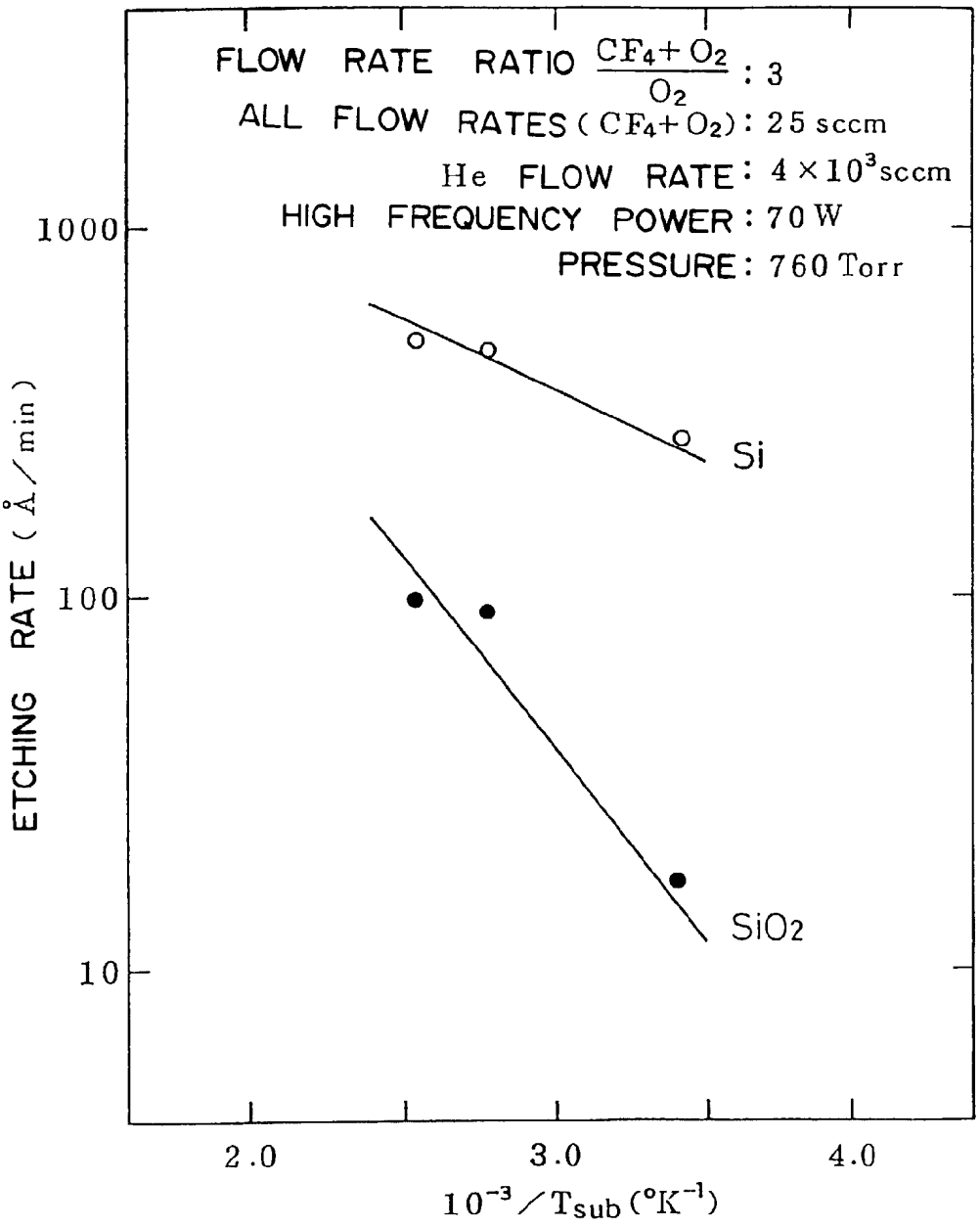
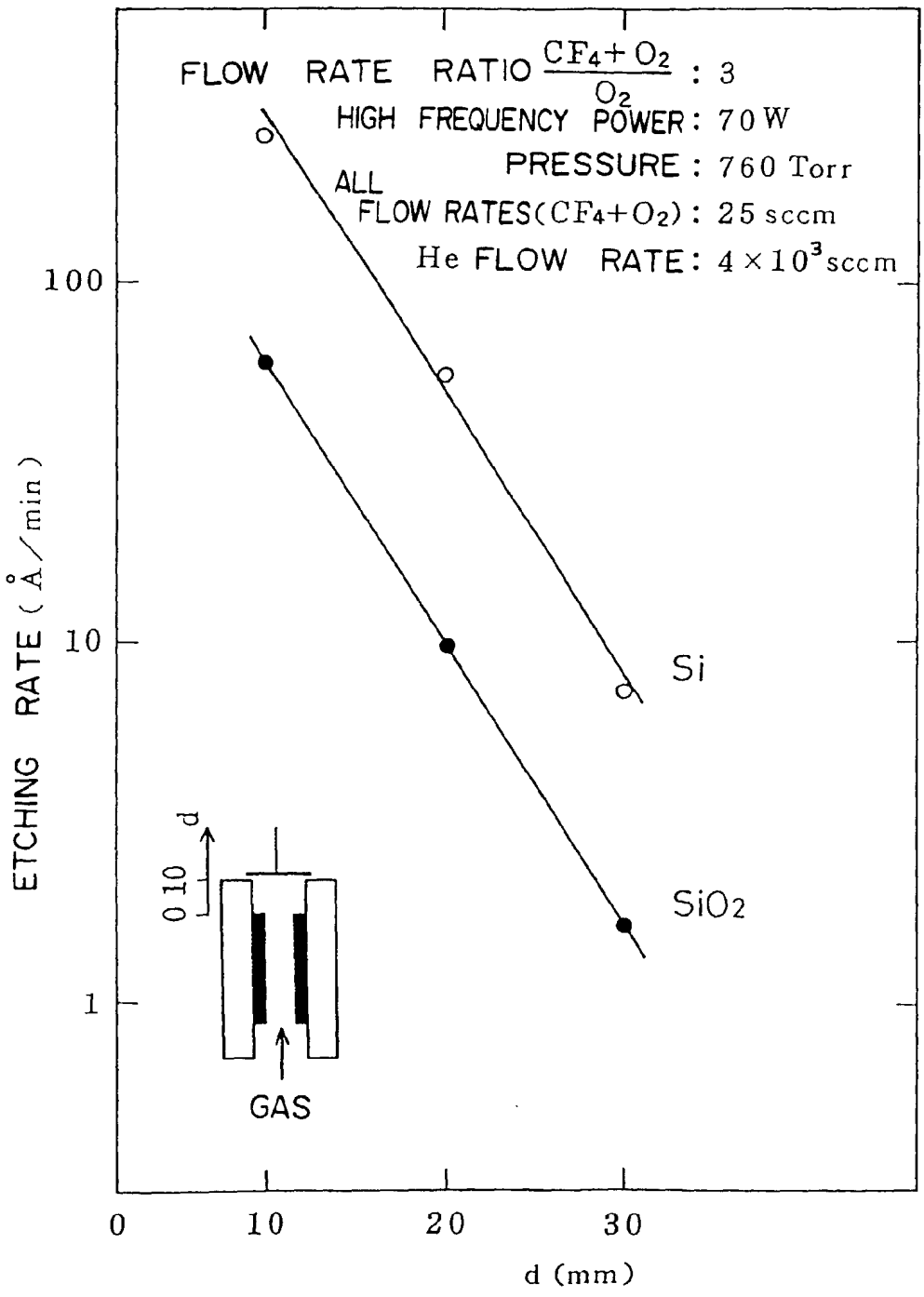

FLOW RATE RATIO $\frac{CF_4+O_2}{O_2}$: 3
ALL FLOW RATES (CF_4+O_2) : 25 sccm
He FLOW RATE : 4×10^3sccm
HIGH FREQUENCY POWER : 70 W
PRESSURE : 760 Torr
1000
100
10
ETCHING RATE (Å/min)
Si
SiO2
2.0
3.0
4.0
$10^{-3}/T_{sub}$ ($°K^{-1}$)

FIG. 7


FLOW RATE RATIO $\frac{CF_4+O_2}{O_2}$: 3
HIGH FREQUENCY POWER: 70 W
PRESSURE: 760 Torr
ALL FLOW RATES(CF_4+O_2): 25 sccm
He FLOW RATE: 4×10^3 sccm
ETCHING RATE (Å/min)
100
10
1
Si
SiO_2
0 10 d
GAS
0
10
20
30
d (mm)